

**OFFICE OF NAVAL RESEARCH**

Grant or Contract N00014-95-1-0302  
PR# 97PR02146-00

Technical Report No. 331

**Experimental and Theoretical Study of Ring Substituent Induced  
Effects on the Structure and Optical Properties of Poly (*p*-  
pyridylvinylene-phenylvinylene)s**

by

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Submitted to

Journal of Chemical Physics

The Ohio State University  
Department of Physics  
Columbus, OH

**DTIC QUALITY INSPECTED 2**

February 6, 1998

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19980227 080

## REPORT DOCUMENTATION PAGE

Form Approved OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington DC 20503

1. AGENCY USE ONLY (Leave blank)

2. REPORT DATE

2/3/98

3. REPORT TYPE AND DATES COVERED

Technical

4. TITLE AND SUBTITLE

Experimental and Theoretical Study of Ring Substituent Induced Effects  
on the Structure and Optical Properties of Poly (*p*-pyridylvinylene-phenylenevinylene)s

5. FUNDING NUMBERS

N00014-95-1-0302

6. AUTHOR(S)

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7. PERFORMING ORGANIZATION NAMES AND ADDRESS(ES)

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8. PERFORMING ORGANIZATION REPORT NUMBER

P331

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Office of Naval Research  
800 N. Quincy Street  
Arlington, VA 22217

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

Submitted to Journal of Chemical Physics

12a. DISTRIBUTION/AVAILABILITY STATEMENT

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12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

Optical absorption and photoluminescence spectroscopy have been carried out on a new class of (phenylene) ring substituted *p*-pyridylvinylene-phenylenevinylene polymers used as active material in light-emitting diodes. The effects of the ring substitutions on the optical absorption and photoluminescence energies are qualitatively explained through the use of semi-empirical quantum chemical modeling of the ring torsion angle. Reduced aggregation through the use of so-called strap substituents on the phenylene rings is also discussed.

14. SUBJECT TERMS

spectroscopy, optical absorption, photoluminescence, *p*-pyridylvinylene-phenylenevinylene, 21  
polymers, ring-substituted

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASS. OF RPT

Unclassified

18. SECURITY CLASS. OF THIS PG.

Unclassified

19. SECURITY CLASS. OF ABSTRACT.

Unclassified

20. LIMITATION OF ABSTRACT

Unlimited

# Experimental and Theoretical Study of Ring Substituent Induced Effects on the Structural and Optical Properties of Poly(*p*-pyrildylvinylene-phenylenevinylene)s

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## Abstract

Optical absorption and photoluminescence spectroscopy have been carried out on a new class of (phenylene) ring substituted *p*-pyrildylvinylene-phenylenevinylene polymers used as active material in light emitting diodes. The effects of the ring substitutions on the optical absorption and photoluminescence energies are qualitatively explained through the use of semi-empirical quantum chemical modeling of the ring torsion angle. Reduced aggregation through the use of so called strap substituents on the phenylene rings also is discussed.

## I. Introduction

Since the report<sup>1</sup> in 1990 of a conjugated polymer-based light emitting diode (LED) with poly(*p*-phenylenevinylene) (PPV) as the active layer, there have been various improvements in the device design including use of multi layered structures<sup>2</sup> and blends<sup>3</sup> to obtain exciton confinement and hence improved efficiency of the diodes. Other design improvements include color variable,<sup>4,6</sup> AC-driven<sup>7</sup> and flexible devices.<sup>8</sup>

Much effort has also gone into the synthesis and use of new light-emitting polymers in these devices.<sup>9-12</sup> Recently, a new class of poly(*p*-pyrildylvinylene phenylenevinylene) (PPyVPV) based polymers have been synthesized<sup>13</sup> and used in a wide variety of light emitting diodes.<sup>5,14-16</sup> Promising new devices have been fabricated using these polymers in combination with poly(vinylcarbazole) (PVK) where the formation of exciplexes was found to enhance the luminescence efficiency.<sup>14,15</sup> The exciplex formation takes place in both multi layers and polymer blends.

In order to improve the solubility of the PPyVPV polymers, various ring substituents are used, typically alkyl and alkoxy chains.<sup>13</sup> Lately, continuous chains labeled here as "straps", attached at the 2,5

ortho positions of the phenylene rings, have been used to decrease aggregation in films. States formed due to aggregation tend to quench luminescence and hence reduce the efficiency of the LEDs.<sup>23</sup> Adding substituents to the phenylene rings can effect the electronic structure, both directly by withdrawing or donating charge thereby lowering or raising the energy bands, and indirectly by steric hindrance induced ring torsion.<sup>17,18</sup> The latter effect is of particular importance since ring torsion strongly effects the optical band gap and thus the wavelengths of the absorption and luminescence. The overlap of the  $p_z$  orbitals along the (conjugated) polymer back bone is decreased as the inter ring torsion angle,  $\theta$ , is increased.<sup>17,18</sup> Also, a decrease in  $p_z$  overlap will cause a decrease in the dispersion of the HOMO and LUMO bands, a larger band gap and blue-shifted optical absorption maximum.<sup>18</sup> The photoluminescence maximum may be less effected by inter-ring torsion, as the excitons will tend to migrate to the lowest energy segment of a polymer chain, *i.e.*, the most planar one, before recombining and emitting light.<sup>18</sup> Thus photoluminescence is associated with the most planar segments of a polymer, where as optical absorption gives an average of the various band gaps/ring torsions of the polymer solution or film. In this paper we present the absorption and luminescence data of an extensive series of PPyVPV and strapped PPyVPV copolymers. We also present results of quantum chemical modeling of trimers representative of the copolymers. The theoretical results account for the absorption and luminescence data of the polymers obtained from solutions and films, and demonstrate the importance of oxygen in the side groups in stabilizing the planarity of the polymer chains.

## II. Theoretical Methodology

The use of quantum chemical modeling to study the effects of ring torsion in conjugated polymers is well established.<sup>19</sup> The geometry optimizations were carried out using the Austin Model 1 semiempirical technique.<sup>20</sup> We choose this method because previous studies on phenylene and polyene chains have shown that the AM1 method gives good agreement for bond lengths, as well as for torsion angles and potentials, with data obtained from experiment and Hartree-Fock *ab initio* calculations.<sup>21,22</sup> Specifically, in the case of *trans*-stilbene,<sup>21</sup> the AM1 torsion potential curves have very similar shapes to those of Hartree-Fock 3-21G curves, the main difference lying in the fact that the AM1 barriers are lower (by about a factor of 2). In this work, the torsion potential curves were obtained using the rigid rotor approximation, *i.e.*, the optimized geometry was kept fixed except while the two ring torsion angles were changed in steps of 15 degrees. The rigid rotor approximation gives results qualitatively in line with fully relaxed AM1 calculations but overestimates the torsion potentials for conformations with high steric

hindrance.<sup>23</sup> The size of the molecules used in the torsion potential calculations (three-ring oligomers, see Fig.1 a-e) prevented us from performing Hartree-Fock *ab initio* calculations at a level that would have given us substantially better quality results.

In the calculations discussed below, the ring involved in the torsion was rotated back and forth, keeping the two end rings in the same plane. We also carried out calculations where the rings were rotated in the same direction creating a 'cork-screw' conformation, and the difference in energy was found to be less than 0.1 kcal/mol for the same torsion angle. This is consistent with the case of *trans*-stilbene, where the difference in energy between  $C_2$  and  $S_2$  symmetries is lower than 0.3 kcal/mol.<sup>21</sup> Note that unlike the case of *trans*-stilbene, there are two different types of ring twisting that can occur. Rotation of a phenylene ring will lead to different types of steric hindrance than the rotation of a pyridine ring. Hence, there is a need to study the two cases separately. In all cases, the calculated torsion potentials are for the rotations around two bonds (separate calculations showed that the rotation around a single bond gives roughly half the potential barrier due to the rotation around two bonds, as was also the case for *trans*-stilbene<sup>21</sup>).

### III. Experimental Methodology

The synthesis of the PPyVPV copolymers is described elsewhere<sup>13</sup>. All of the PPyVPV copolymers are soluble in common organic solvents such as tetrahydrofuran (THF), xylene, and chloroform. The photoluminescence (both film and solution) measurements were made using a PTI QM1 luminescence spectrometer. A Xenon arc lamp was used as the excitation source and the wavelengths of the photons were chosen so as to coincide with the peak of the absorption. The resolution of the photoluminescence spectra were 1 nm. Light from the arc lamp did not cause damage to the polymers. The absorption measurements were made using a Perkin Elmer Lambda 19 UV/Vis/NIR spectrometer with a resolution of 2 nm. The film samples were spin cast (~1000 rpms) on quartz from xylene (~ 5-10 mg/ml) solutions resulting in 400-500 Å thick films. Very dilute solutions ( $<10^{-5}$  M) of the PPyVPV copolymers in xylene were used for the solution photoluminescence and absorption measurements.

### IV. Theoretical Results

#### A. Fully optimized bond lengths and bond angles.

In Table I, AM1-optimized bond lengths and bond angles are presented for both the fully optimized cases of the ring substituted trimers (a), (b), (c) and (d) in Fig. 1, as well as for the

unsubstituted three-ring molecule (e). The ring substitutions slightly increase the bond lengths between the substituted carbons and the adjacent carbon atoms. Note that these effects on bond lengths are local, *i.e.*, only the bonds adjacent to the substituted atom are significantly affected, with the pyridine ring and vinylene bond lengths being approximately the same for all cases.

The substitutions also affect the bond angles of the polymer backbone. The  $\angle(\text{C2-C3-C4})$  bond angle is significantly larger for (a), (b) and (d) than for (c) and (e). The increase in angle is due to steric interaction between the ring substituent and the hydrogen attached to C4. The  $\angle(\text{C3-C4-C5})$  and  $\angle(\text{C3-C4-H})$  bond angles also are affected by the ring substitution, causing the C4 hydrogen atom to move towards the substituent group for case (c) and away from the substituent group for cases (a) and (b) as compared to (e). The largest bond angle modifications occur for case (b), consistent with the fact that it has the largest inter ring torsion angle,  $32.3^\circ$ , signifying the greatest steric interaction between the ring substituent and the C4 hydrogen. Note that for the case (b), angles  $\angle(\text{C2-C11-O1})$  and  $\angle(\text{C3-C2-C11})$  are significantly larger than  $120^\circ$  in order to reduce the steric hindrance between the C4 hydrogen and the carbonyl oxygen O1. However, for the case of dimethoxy substitution, (c), the  $\angle(\text{C3-C2-O})$  angle is decreased to  $115.4^\circ$  due to the formation of a weak hydrogen bond between the methoxy oxygen and the C4 hydrogen.<sup>21</sup>

## B. Torsion potentials

The torsion potential curve associated with rotation of a pyridine ring surrounded by two vinylene-phenylene groups is shown in Fig. 2. The middle (pyridine) ring is rotated while the end phenylene rings are kept in the same plane as the vinylene groups. Compared to the lowest energy conformation with a torsion angle of  $5^\circ$ , the barrier towards a coplanar conformation is less than 0.1 kcal/mol, and the torsion potential curve in the region between  $+30^\circ$  to  $-30^\circ$  is quite flat. The barrier towards  $0^\circ$  torsion is so small that solid state packing is likely to drive the trimer/polymer into a coplanar conformation in films like the case for PPV<sup>22</sup> and stilbene.<sup>21</sup> The barrier towards a  $90^\circ$  rotation is 3.8 kcal/mol, roughly the same as that of *trans*-stilbene, 3.4 kcal/mol.<sup>21</sup> The torsion potential curve for rotation of the pyridine rings are not effected by the substituents on the phenylene rings and will hence not be discussed separately for the various trimers/polymers studied. The case for rotating the phenylene ring while keeping the end pyridine rings in the same plane as the vinylene groups (Fig. 1e) is approximately equivalent to the case of *trans*-stilbene and PPV, where the barrier towards a coplanar conformation is less than 0.4 kcal/mol and solid state packing is found to cause a coplanar conformation when the polymer is spun or cast as a film.<sup>17,21</sup>

We now turn to the trimer where the phenylene ring is substituted by two ethyl groups (Fig. 1a); the corresponding torsion potential curves are displayed in Fig. 3. For rotation of the phenylene ring, the barrier towards a coplanar conformation is 2.0 kcal/mol, with the global minimum at 30.5°. There also is a sharp local minimum at 135° torsion angle. The steric interactions between the ethyl substituents and the vinylene hydrogens adjacent to the phenylene ring are thus substantially larger than those between the phenylene ring hydrogens and vinylene hydrogens of case (e). This is consistent with the analysis of the bond length and angle distortions of case (a) compared with (e). The sharp minima and the high barriers limit the solution torsion angles to |30°| to |45°| and |120°| to |135°| respectively with solid state packing unlikely to cause a significant change in torsion angles going from solution to film. Since the local minimum at |135°| is 2.6 kcal/mol higher than the global minimum at |30.5°|, the latter conformation should dominate both in solution and in films.

Next, we consider the trimer where the rings are substituted by two formyl groups, Fig 1b. The torsion potential curves associated with rotation of the middle ring is shown in Fig. 4. The barrier towards a coplanar conformation is 0.8 kcal/mol for the case of the double bonded oxygen sterically interacting with the vinylene hydrogen. The relatively low barrier would suggest that angles between |15°| to |35°| are present in films due to solid state packing. In solution, the torsion angle will be approximately that of its energy minimum, ~32°. The substituent groups may also be rotated relative to the plane of the phenylene ring. In Fig 5, the torsion potential curve is depicted for rotation of two substituent groups in an otherwise coplanar conformation. Torsion of 0° represents the case of the carbonyl and methoxy oxygen being in the same plane as the trimer backbone and the carbonyl oxygen pointing towards the phenylene hydrogen. Two minima exists, the one at |45°| being 0.12 kcal/mol higher than the global minimum at |150°|, *i.e.*, the carbonyl oxygen pointing towards the vinylene hydrogen at a 30° angle to the trimer backbone plane. The barrier towards planar conformation is 1.9 kcal/mol from the global minimum and 10.9 kcal/mol from the local minimum. This suggests that the case of the carbonyl oxygen pointing in the direction of the vinylene hydrogen is predominant. Indeed, the barrier towards a coplanar conformation along the polymer back bone increases to 3.7 kcal/mol if the formyl groups are rotated in such a way as to have the carbonyl oxygen point towards the phenylene hydrogen.

In Fig. 6, the torsion potential curve for the dimethoxy substituted trimer (c) is depicted. The barrier towards a coplanar conformation is 0.13 kcal/mol, low enough to be overcome by solid state packing. The torsion angle for the fully optimized geometry was found to be ~1°, so a coplanar conformation is likely to be found in solution as well. The low barrier is due to a weak hydrogen bond

being formed between the methoxy oxygen and the C4 hydrogen, locking the geometry into a coplanar conformation as is the case for dimethoxy substituted *trans*-stilbene<sup>21</sup> and dimethoxy-substituted PPV.<sup>17</sup>

The molecule shown in Fig. 1d has an alkoxy strap attached to the 2,5 *ortho* positions of the phenylene ring. The oxygens attached to the *ortho* carbons of the phenylene rings are chemically similar to the methoxy oxygens of Fig 1c, and hydrogen bonding could thus be expected to take place between these oxygens and the vinylene hydrogens. However, as shown in Fig. 7, the barrier towards 0° ring torsion is 1.5 kcal/mol, larger than the case of (c). The region between |10°| to |35°| is quite flat, so torsion angles as low as |10°| are likely to be found in films due to solid state packing. The fully optimized geometry gives the torsion angle as 24.2°, larger than the case for (c), but smaller than cases (a) and (b).

## V. Experimental results and discussions

In Fig. 8 are depicted the photoluminescence (circles) and absorption (triangles) spectra for the PPyVPV polymers as well as their geometrical structure. Solution spectra (open symbols) and spectra from spun films (filled symbols) are shown for all polymers. Values in eV for the absorption and photoluminescence maxima along with the absorption edges are given in Table II.

We first note that the absorption data agree with the behavior derived from the calculations for both the films and the solutions. Polymers (b) and (a) have the highest absorption maxima in solution followed by (da), (d), (dc) and (c), in agreement with the torsion angle calculations, though (d) had a slightly higher maximum than (da). The shift in absorption maximum going from solution to film for polymer (b) (3.08 eV to 2.95 eV) agrees with the flat torsion potential region between |35°| to |15°| and the relative low (0.8 kcal/mol) barrier towards coplanarity. A similar shift for polymer (d) (0.15 eV) is also attributed to the flatness of the torsion potential curve between |35°| to |10°|. Lesser shifts are expected for (dc) and (da) since the band gap is partly determined by the dialkoxy and dialkyl substituted phenylene rings and these are not expected to be significantly effected by solid state packing effects due to the shape of their torsion potential curves. The experimental data gives a shift of 0.09 eV for (dc) and 0.03 eV for (d) in qualitative agreement with our theoretical modeling. We expect no significant shift for (a) and (c) as mentioned above, since (c) has an optimal torsion angle of |1°| in solution, *i.e.*, coplanar, and (a) has a very sharp minimum at ~|30°| with a significant (2.0 kcal/mol) barrier towards coplanarity that is unlikely to be overcome by solid state packing as mentioned previously. The experimental shifts were found to be 0.03 eV, substantially smaller than those for (b) and (d) as expected.



The photoluminescence maxima are expected to follow the same trend in solution as the absorption maxima, though the difference in energy should be smaller due to exciton migration to the most planar/lowest energy segments of the polymers as mentioned in the introduction. The experimental data are in qualitative agreement with the theoretical predictions based on the inter-ring torsion angles with polymers (b) and (a) having the highest PL maxima followed by (da), (d), (dc) and (c). The difference in PL energy between (b) and (c) is also lower as expected, 0.17 eV, as compared to 0.44 eV for the difference in the absorption maxima in solution. Inspecting the absorption data going from solution to film, we see that the low energy tail of the absorption peaks are extended for the film data. By comparing the energy of the position where the intensity is 20% of the absorption maximum, ABS EDGE in Table II, the shift between the solution and film data is found to be significantly larger for the unstrapped cases, suggesting the presence of a greater number of aggregation states in these films.<sup>24</sup> The experimental photoluminescence maxima vary as (da), (dc), (d), (a), (b) and (c) going from highest PL energy to lowest, not well correlated with predictions. It is noted that the strap-substituted polymers are the ones deviating from the expected trend and that all the film PL energies are substantially lower than the solution data which can only in small part be explained by solid state packing effects. Comparing the absorption spectra of (a) and (da), the shifts in going from solution to film are 0.16 eV and 0.03 eV respectively; (c) and (dc) 0.63 eV vs. 0.13 eV. The same trend is found in the photoluminescence data. Going from solution to film the PL shifts are: 0.54 eV vs. 0.38 eV for (a) and (da), 0.58 eV vs. 0.33 eV for (c) and (dc). Hence, the aggregation effects are greatly reduced by the strap substituents. This reduction in aggregation should enhance the luminescence efficiency in films.<sup>24</sup>

## VI. Conclusions

Optical absorption and photoluminescence spectroscopy have been carried out on a new class of (phenylene) ring substituted *p*-pyrildylvinylene-phenylenevinylene polymers used as active material in light emitting devices. The effects of the ring substitutions on the optical absorption and photoluminescence energies have been qualitatively explained through the use of semi-empirical quantum chemical modeling of the inter-ring torsion. Substituents such as alkyl and formyl chains sterically interact with the hydrogens of the vinylene units, causing an increase of the inter-ring torsion and hence increases in the band gap, optical absorption and photoluminescence energies. Since excitons migrate to the lowest energy/band gap segments of the polymers before recombining, the effects are less pronounced for the photoluminescence spectra than the absorption spectra. Alkoxy substituents, however, were found

to induce a coplanar conformation through the formation of weak hydrogen bonds between the alkoxy oxygens and the vinylene hydrogens. The effect of strap substituents on the phenylene rings is similar to that of alkoxy groups while also reducing aggregation in the polymer films.

## VII. Acknowledgments

The authors thank Dr. Yanzhang Wang for discussions. This research was supported in part by ONR. MF also thanks AFSOR and the Swedish Natural Sciences Research Council (NFR) for financial support.

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## Table captions

Table I. AM1-optimized bond lengths (in Å) and bond angles (in °) of the five oligomers shown in Fig. 1.

Table II. Absorption maxima, photoluminescence maxima and absorption edges (20% of maximum) in eV for films and solutions of polymers a, b, c, d, da and dc depicted in Fig. 8.

## Figure captions

Fig. 1. The molecular structures of three-ring oligomers of (a) diethyl-substituted poly(*p*-pyrildylvinylene-phenylenevinylene); (b) diformyl-substituted poly(*p*-pyrildylvinylene-phenylenevinylene); (c) dimethoxy-substituted poly(*p*-pyrildylvinylene-phenylenevinylene); (d) (alkoxy) strap-substituted poly(*p*-pyrildylvinylene-phenylenevinylene) and (e) unsubstituted poly(*p*-pyrildylvinylene-phenylenevinylene).

Fig. 2. Potential energy curves associated with torsion of the middle pyridine ring in a phenylenevinylene-pyridine-vinylene-phenylene trimer. All energies are given relative to that of the fully optimized conformation.

Fig. 3. Potential energy curves associated with torsion of the diethyl-substituted middle (phenylene) ring of trimer (a). All energies are given relative to that of the fully optimized conformation.

Fig. 4. Potential energy curves associated with torsion of the diformyl-substituted middle (phenylene) ring of trimer (b). All energies are given relative to that of the fully optimized conformation.

Fig. 5. Potential energy curves associated with torsion of the formyl groups on the middle (phenylene) ring. The trimer backbone is kept planar and the energies are given relative to the lowest energy conformation.

Fig. 6. Potential energy curves associated with torsion of the dimethoxy-substituted middle (phenylene) ring of trimer (c). All energies are given relative to that of the fully optimized conformation.

Fig. 7. Potential energy curves associated with torsion of the alkoxy-strap-substituted middle (phenylene) ring of trimer (d). All energies are given relative to that of the fully optimized conformation.

Fig. 8. Photoluminescence (circles) and absorption (triangles) spectra for a group of phenylene ring substituted *p*-pyrildylvinylene-phenylenevinylene polymers, geometrical structure given. Solution spectra (open symbols) and spectra from spun films (filled symbols) are shown for all polymers: (a), (b), (c), (d), and (e).

|                  | a      | b      | c      | d      | e      |
|------------------|--------|--------|--------|--------|--------|
| r (C1-C2)        | 1.3959 | 1.3980 | 1.3964 | 1.3978 | 1.3904 |
| r (C2-C3)        | 1.4105 | 1.4088 | 1.4171 | 1.4118 | 1.4044 |
| r (C3'-C1)       | 1.4000 | 1.4030 | 1.4000 | 1.4000 | 1.4030 |
| r (C3-C4)        | 1.4555 | 1.4544 | 1.4504 | 1.4518 | 1.4525 |
| r (C4-C5)        | 1.3439 | 1.3441 | 1.3448 | 1.3438 | 1.3441 |
| r (C5-C6)        | 1.4494 | 1.4487 | 1.4483 | 1.4490 | 1.4480 |
| r (C6-C7)        | 1.4173 | 1.4175 | 1.4190 | 1.4150 | 1.4189 |
| r (C7-N)         | 1.3437 | 1.3433 | 1.3429 | 1.3448 | 1.3429 |
| r (N-C8)         | 1.3479 | 1.3483 | 1.3484 | 1.3469 | 1.3484 |
| r (C8-C9)        | 1.4061 | 1.4059 | 1.4055 | 1.4070 | 1.4056 |
| r (C9-C10)       | 1.3945 | 1.3947 | 1.3948 | 1.3932 | 1.3948 |
| r (C10-C6)       | 1.4030 | 1.4030 | 1.4030 | 1.4060 | 1.4030 |
| r (C4-H)         | 1.1045 | 1.1059 | 1.1064 | 1.1060 | 1.1046 |
| r (C2-C11)       | 1.4896 | 1.4748 |        |        |        |
| r (C11-C12)      | 1.5072 |        |        |        |        |
| r (C2-O)         |        |        | 1.3847 | 1.3913 |        |
| r (O-C11)        |        |        | 1.4220 | 1.4322 |        |
| r (C11-O1)       |        | 1.2344 |        |        |        |
| r (C11-O2)       |        | 1.3727 |        |        |        |
| r (O2-C12)       |        | 1.4286 |        |        |        |
| ∠ (C4'-C3'-C1)   | 120.3  | 119.8  | 122.4  | 121.5  | 122.2  |
| ∠ (C3'-C1-C2)    | 121.8  | 121.9  | 121.0  | 120.4  | 120.6  |
| ∠ (C1-C2-C3)     | 118.8  | 119.9  | 121.2  | 121.6  | 120.7  |
| ∠ (C2-C3-C4)     | 120.8  | 122.1  | 119.5  | 120.1  | 119.1  |
| ∠ (C3-C4-C5)     | 124.0  | 123.3  | 125.7  | 124.6  | 124.5  |
| ∠ (C4-C5-C6)     | 124.5  | 124.4  | 124.7  | 124.3  | 125.2  |
| ∠ (C3-C4-H)      | 115.6  | 115.4  | 114.2  | 114.3  | 114.6  |
| ∠ (C2-C11-O1)    |        | 129.7  |        |        |        |
| ∠ (C2-C11-O2)    |        | 113.4  |        |        |        |
| ∠ (C3-C2-C11)    | 119.6  | 121.6  |        |        |        |
| ∠ (C2-C11-C12)   | 115.4  |        |        |        |        |
| ∠ (C3-C2-O)      |        |        | 115.4  | 120.8  |        |
| ∠ (C2-O-C11)     |        |        | 116.5  | 114.2  |        |
| ∠ (C1'-C3-C4-C5) | 30.5   | 32.3   | 1.0    | 24.2   | 22.3   |

Table I.

|           | FILM    |          |        | SOLUTION |          |        |
|-----------|---------|----------|--------|----------|----------|--------|
|           | ABS MAX | ABS EDGE | PL MAX | ABS MAX  | ABS EDGE | PL MAX |
| <b>a</b>  | 3.05    | 2.45     | 2.00   | 3.02     | 2.61     | 2.54   |
| <b>b</b>  | 2.95    | 2.40     | 1.97   | 3.08     | 2.61     | 2.56   |
| <b>c</b>  | 2.61    | 2.13     | 1.74   | 2.64     | 2.37     | 2.39   |
| <b>d</b>  | 2.69    | 2.40     | 2.04   | 2.84     | 2.55     | 2.45   |
| <b>da</b> | 2.73    | 2.42     | 2.08   | 2.76     | 2.45     | 2.46   |
| <b>dc</b> | 2.60    | 2.26     | 2.07   | 2.69     | 2.39     | 2.40   |

Table II.

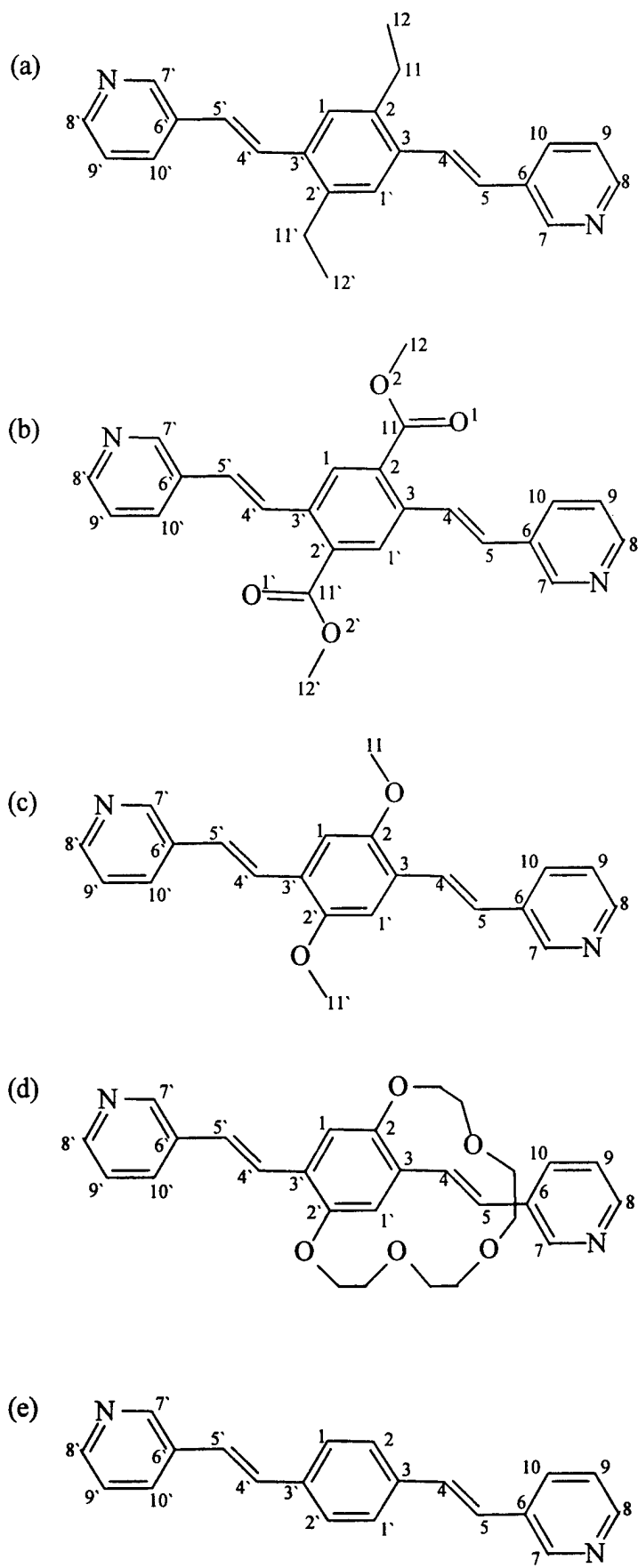


Fig.1



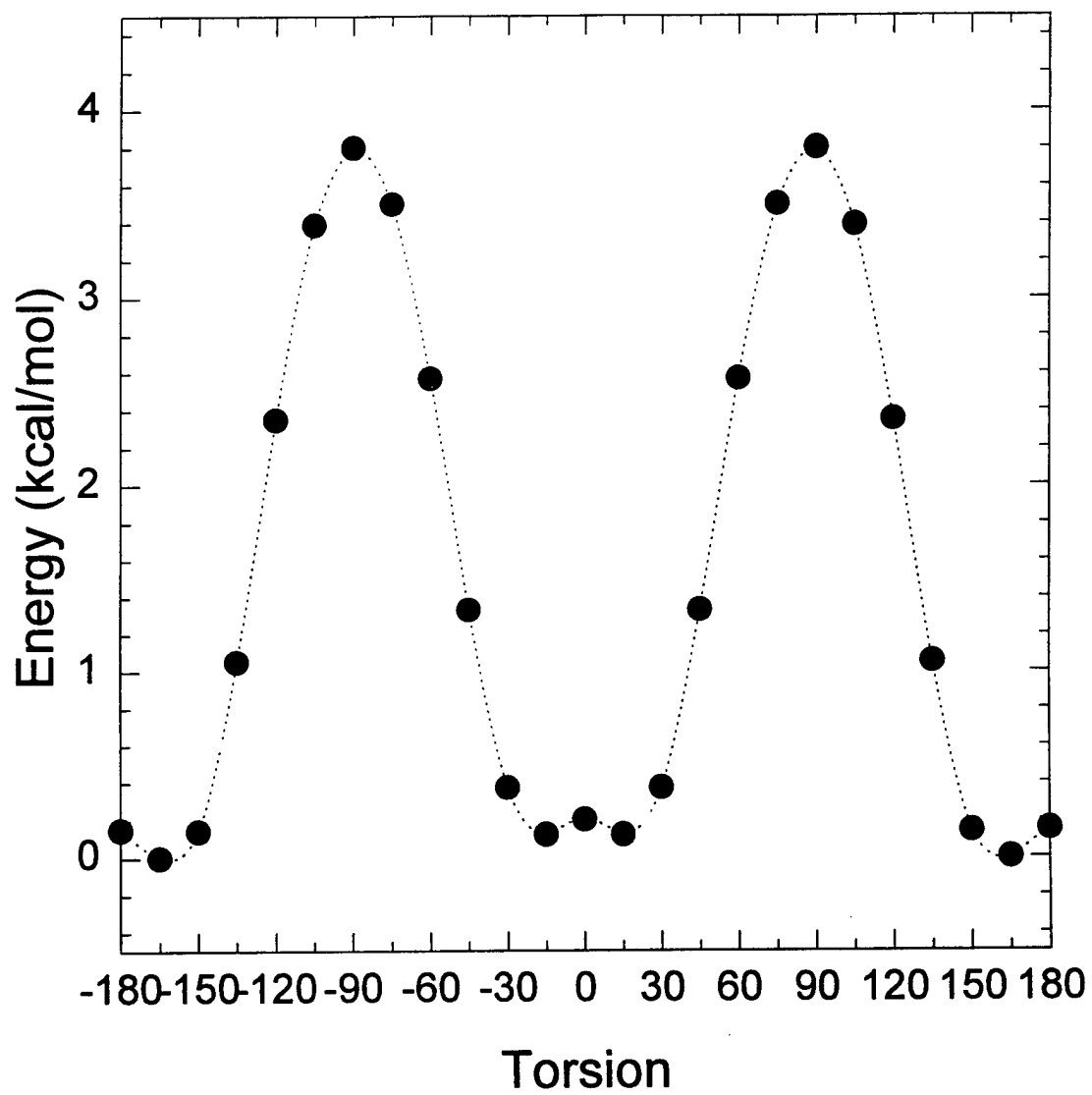


Fig. 2

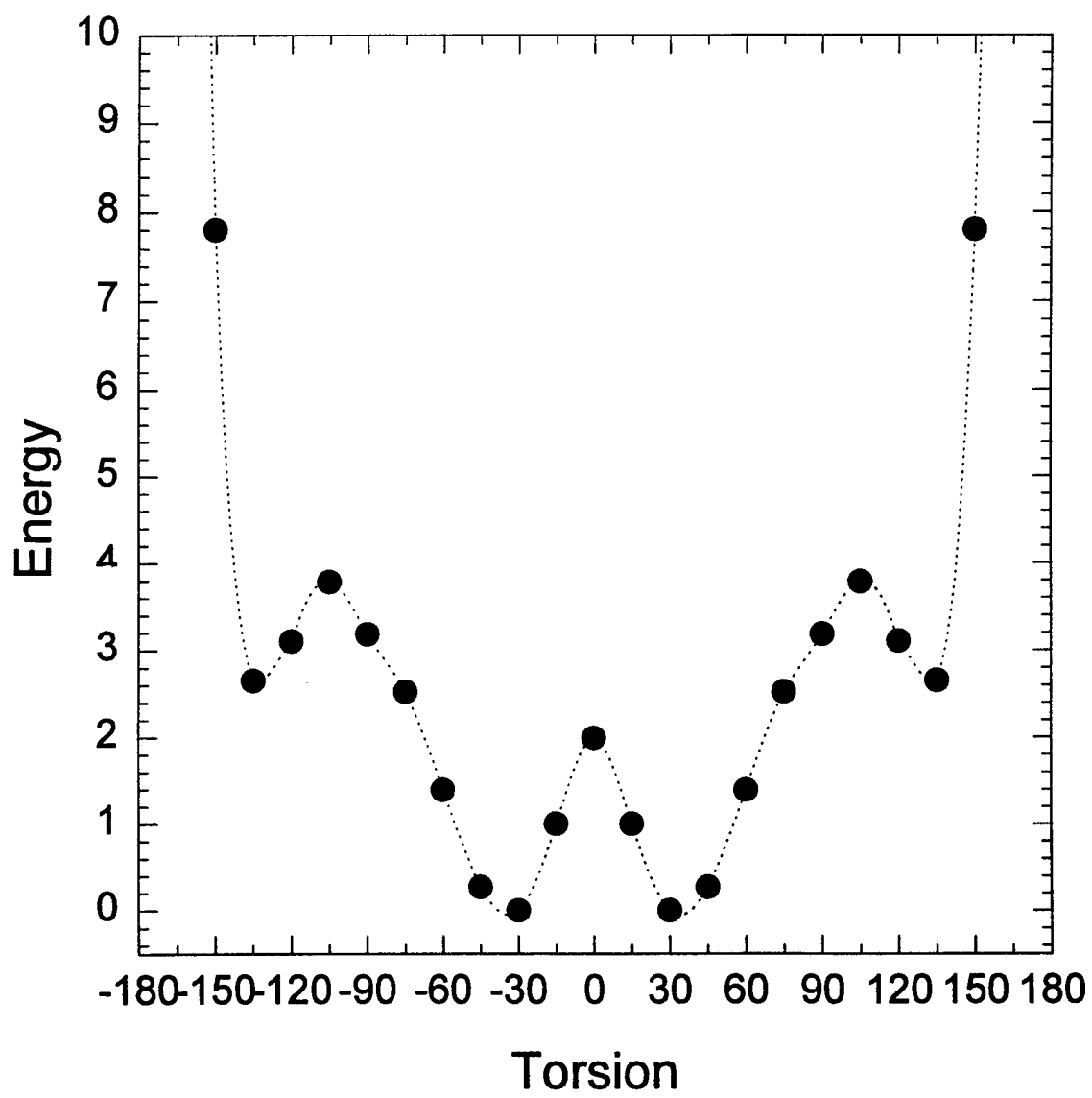


Fig. 3

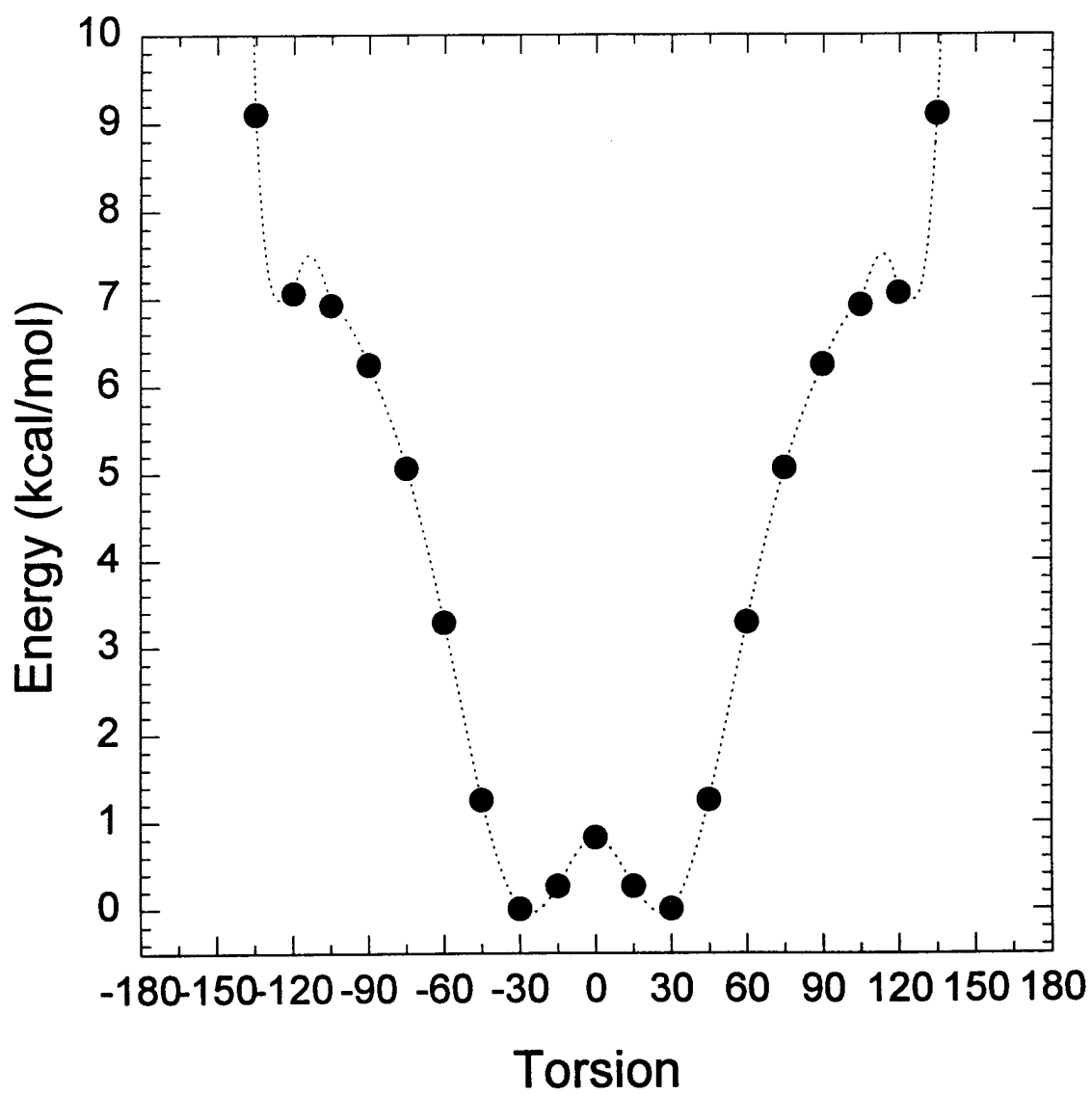


Fig. 4

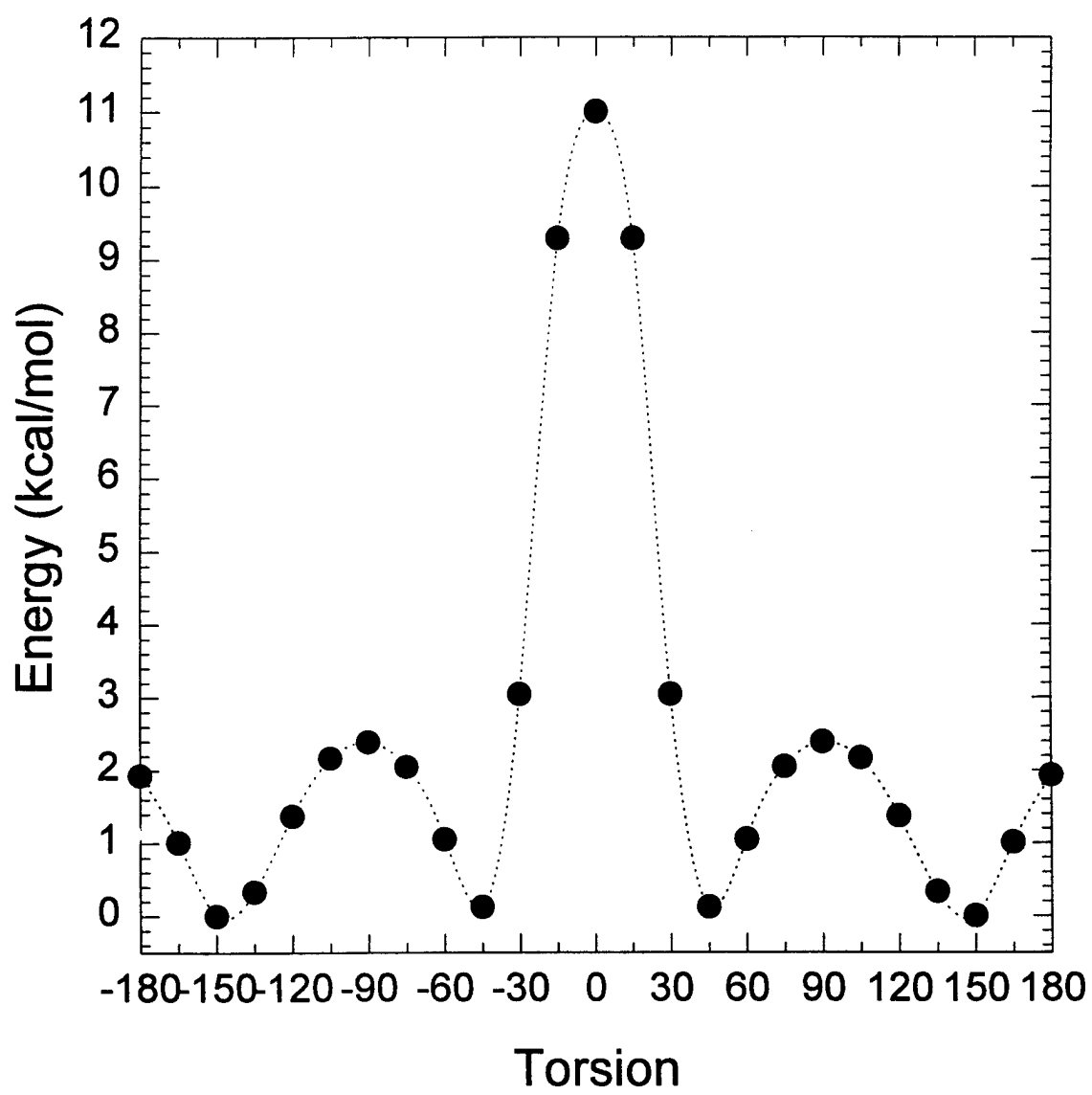


Fig. 5

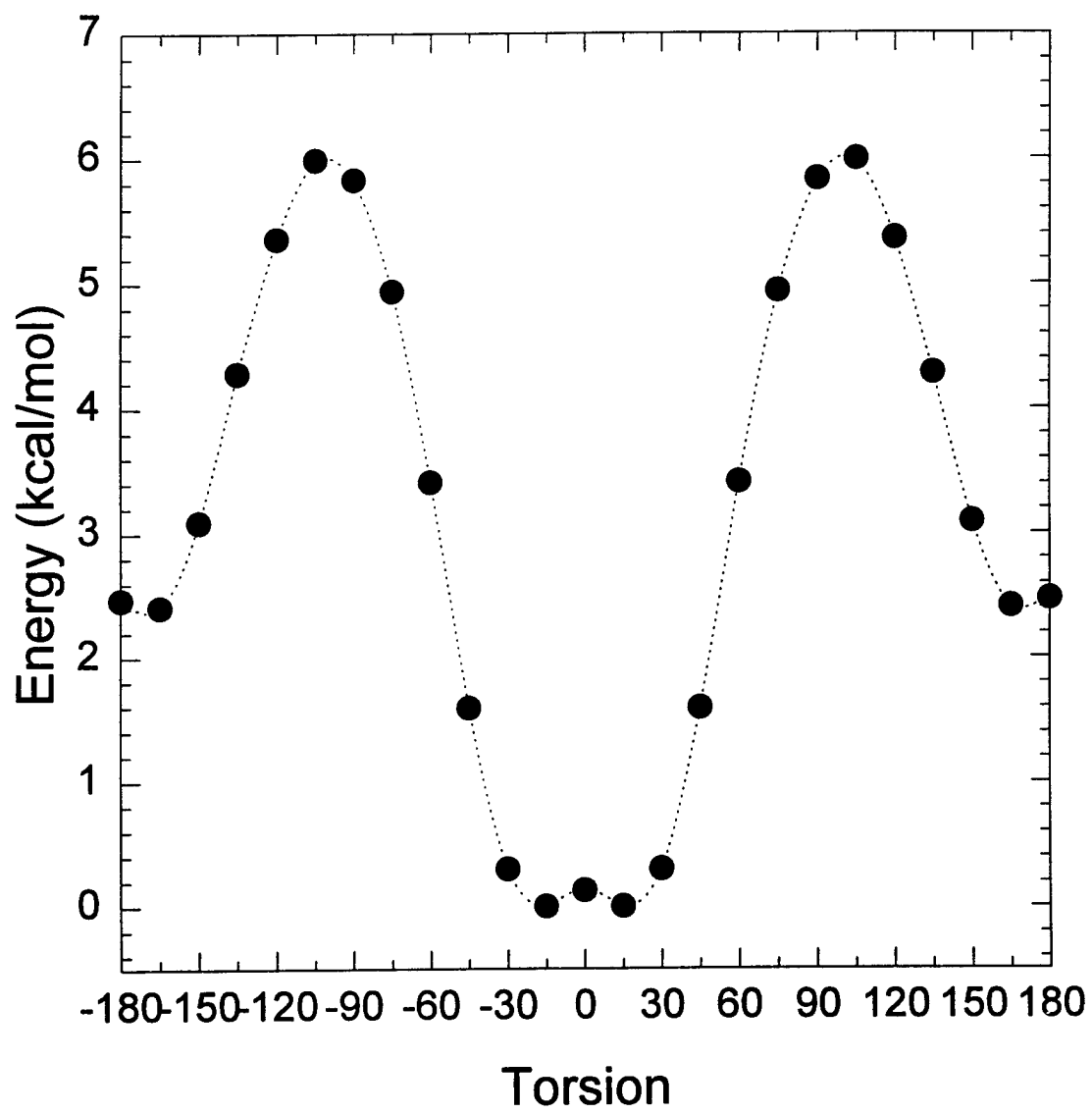


Fig. 6

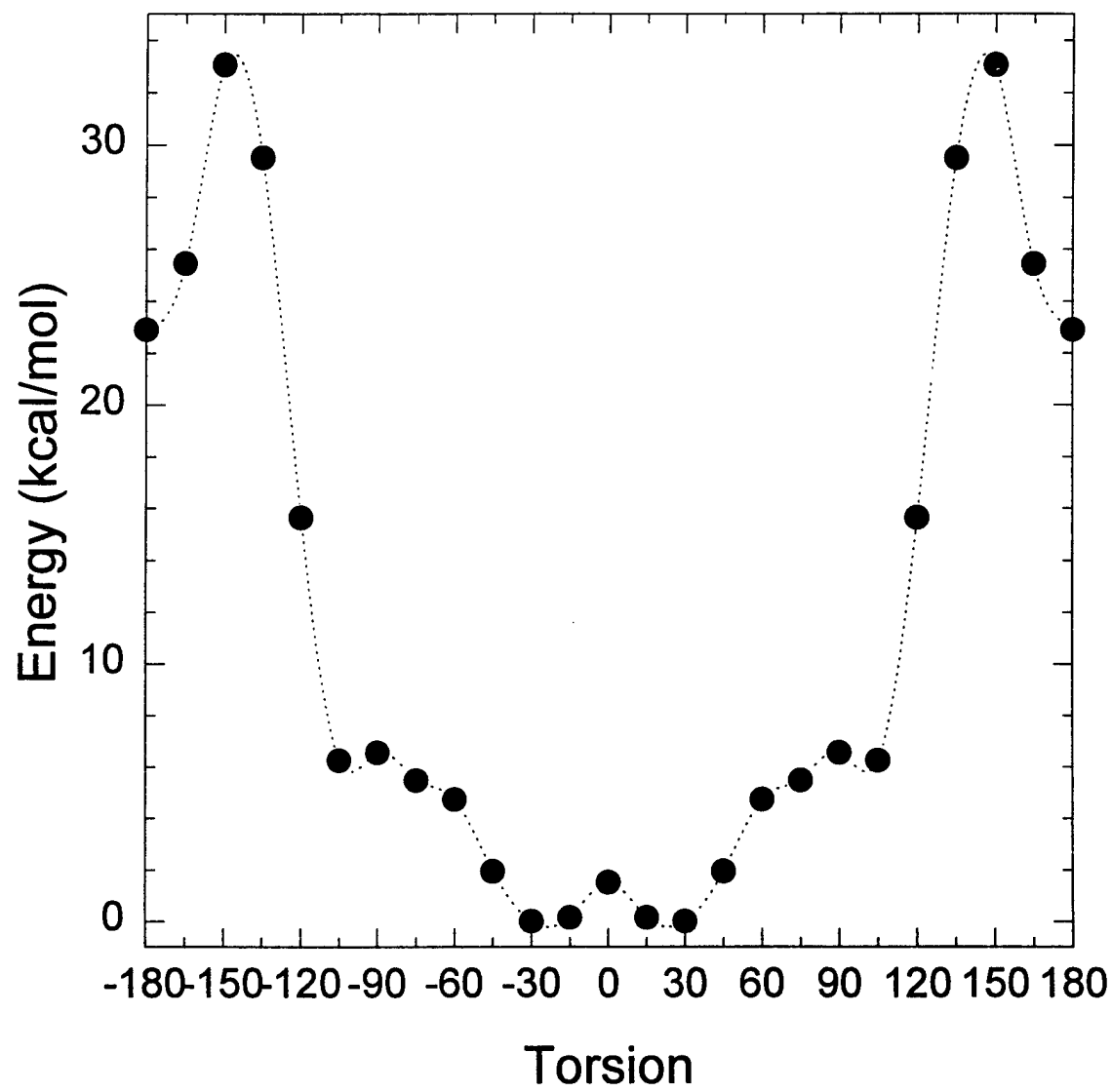


Fig. 7

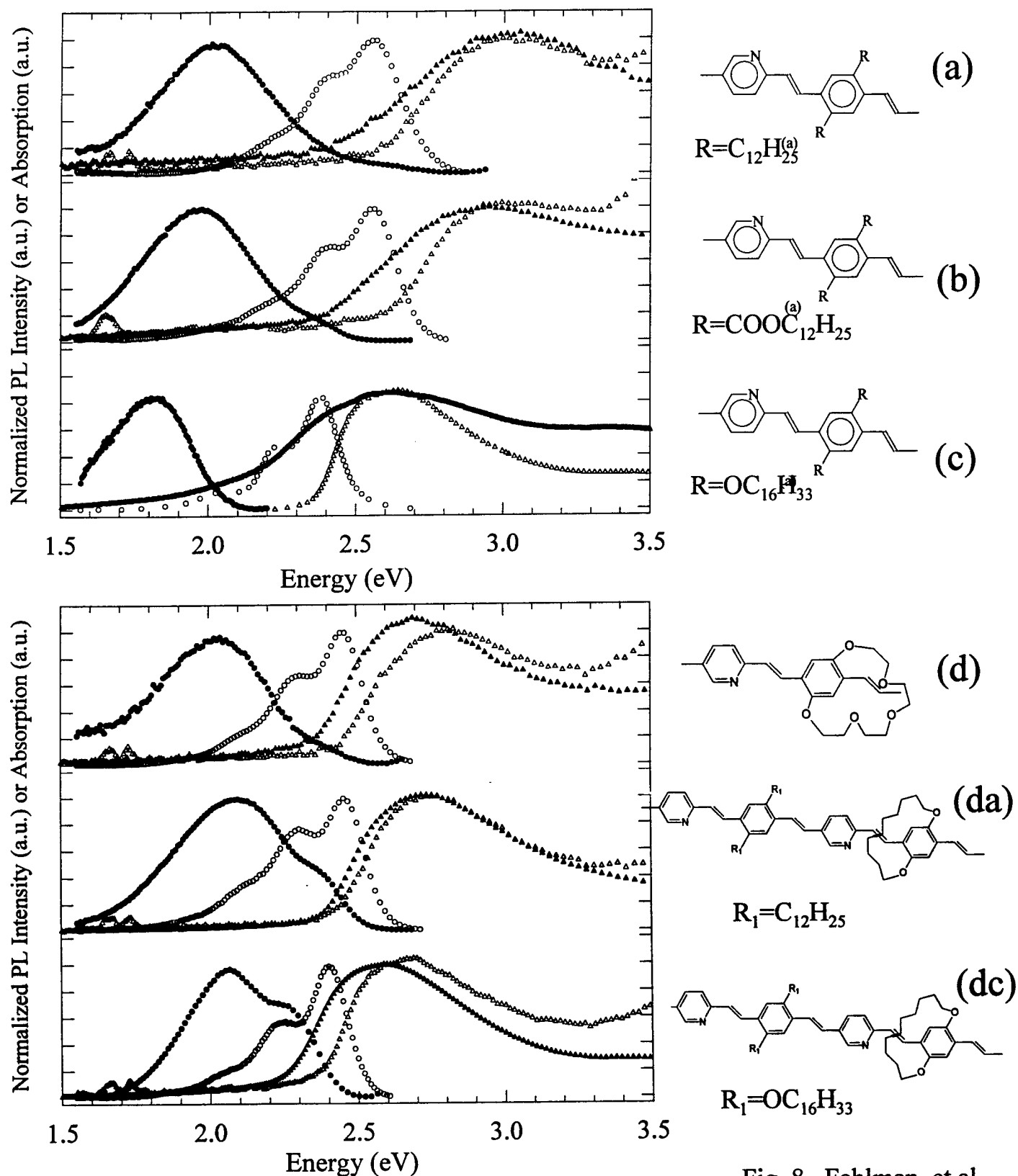


Fig. 8 Fahlman, et al